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Completion of Kr-81 and Kr-85 Analysis Development for Hydrogeology and Testing its Validity by Assessing Aquifer Recharge Rates (July 2001 through June 2006 Reporting Period)

Norbert Thonnard, PhD¹
Principal Investigator

Larry D. McKay, PhD² and Ronald E. Yoder, PhD³
Co-Investigators

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Institute for Rare Isotope Measurements¹
The University of Tennessee
10521 Research Drive, Suite 300
Knoxville, TN 37932

Department of Earth and Planetary Sciences²
The University of Tennessee
Knoxville, TN 37996

Department of Biological Systems Engineering³
University of Nebraska-Lincoln
Lincoln, NE 68583

Summary

The overall objective was to complete the development of a RIMS-based analytical technique to determine the concentration of the rare krypton radioisotopes, ^{81}Kr and ^{85}Kr , in samples of interest to the geoscience and planetary science community

The key to RIMS is the use of tunable lasers to selectively and efficiently excite by resonant photon absorption atomic states unique to the chosen element. Ionization of the specified element can then occur while excluding all other constituents of the sample, bringing detection limits down to the single-atom level. Combining RIMS with several steps of isotopic enrichment makes detection of a rare isotope, such as ^{81}Kr , feasible. A complete process for groundwater samples consists of starting with (1) collecting the groundwater sample, (2) degassing the water sample, (3) separating Kr from the recovered gases, (4 & 5) two isotopic enrichments reducing interfering isotopes by $>10^9$, and (6) detecting the rare krypton isotope using RIMS in a time-of-flight system. Required water sample size is 20 liters for ^{81}Kr and 10 to 3 liters for ^{85}Kr . Weak links in the above steps were to be identified and rectified. Most of the troublesome issues were resolved, but unfortunately, two key difficulties could not be resolved with the available resources, so the overall, final goal of completing a suite of measurements was not achieved.

In spite of this, valuable collaborations were established to demonstrate the value of ^{81}Kr and ^{85}Kr measurements in two critical applications, the future site of a nuclear waste repository, where high efficiency ^{81}Kr measurements would allow groundwater dating of low-yield formations, and a multi-method analysis of potential contamination inflow into a large municipal water system, where the simplicity of interpretation of ^{85}Kr measurements could become a valuable future interpretive tool. Therefore, samples were collected anyway, and processing started using the working parts of the method, so that comparisons to other methods could be made in the future

Introduction

Noble gases have unique properties making them valuable in earth and planetary science research. Being inert, they do not interact chemically with their environment, resulting in significant simplification and less uncertainty in understanding their transport through the earth's atmosphere, hydrosphere and lithosphere, and similarly, in processes on other solar system bodies. Except for argon, noble gases are significantly depleted in the earth's atmosphere relative to other elements. Their low concentration makes analysis more difficult, and hence, has not seen as widespread use as other elements or molecules in research.

At 1.14 ppm, krypton is a trace constituent of the earth's atmosphere. Two of its radioactive isotopes, cosmogenic ^{81}Kr (229 ka half-life, 10^{-13} isotopic abundance) and anthropogenic ^{85}Kr (10.8 a half-life, 10^{-11} isotopic abundance) have long been considered potentially ideal environmental tracers, especially in hydrology, but have seen little use because practical analytical techniques are still not available.

This difficulty is illustrated dramatically by considering ^{81}Kr . As there are less than 1,200 ^{81}Kr atoms in a one-liter modern groundwater sample, decay-counting methods are a practical impossibility, as $>10^7$ liters of water would be required in principle, assuming no background. Tandem-Accelerator Mass Spectrometry, (AMS) which has become a very valuable and almost routine analytical technique for rare radionuclides such as ^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl , ^{41}Ca , and ^{129}I , cannot be used because krypton does not form negative ions.

Due to the much shorter half-life and larger isotopic abundance of ^{85}Kr than ^{81}Kr , measurements are possible using decay counting. Although the few measurements made to date have demonstrated ^{85}Kr 's usefulness in hydrogeology, (Rozanski and Florkowski, 1979; Smethie, et al., 1992; Ekwurzel, et al., 1994) the 120 to 250 liters of groundwater and long (~week) low-level decay counting required for a single measurement have limited its application to a few special cases.

It wasn't until the development of *Resonance Ionization Spectroscopy*, (RIS) a concept that in principle could detect a single atom of one element in an extremely large background of other elements and molecules, that serious consideration was given to utilizing the rare atmospheric ^{81}Kr and ^{85}Kr noble gas isotopes as environmental tracers. The pioneering work on RIS was done in the early 1970s by groups lead by G.S. Hurst at the Oak Ridge National Laboratory (Hurst et al., 1975; Payne et al., 1975) and V.S. Letokhov at the Institute of Spectroscopy (Ambartzumian and Letokhov, 1972) of the Russian Academy of Sciences. The key to RIS is the use of tunable lasers to selectively and efficiently excite by resonant photon absorption atomic states unique to the chosen element. Ionization of the specified element can then occur while excluding all other constituents of the sample, bringing detection limits down to the single-atom level (Hurst et al., 1977). A review by Payne et al. (1994) provides a useful overview of both theoretical and experimental aspects of RIS, as applied to mass spectrometry.

Combining *Resonance Ionization Mass Spectrometry* (RIMS) with several steps of isotopic enrichment made detection of a rare isotope, such as ^{81}Kr , feasible. The first-ever quantitative measurement of ^{81}Kr from a groundwater sample (Thonnard, et al., 1987; Lehmann, et al., 1991)

was made using the method conceived at Oak Ridge National Laboratory (Hurst, et al., 1985; Lehmann, et al., 1985) and put into practice at Atom Sciences, Inc. (Willis et al., 1989) The groundwater measurements were followed by the first-ever age determination of ancient ice using ^{81}Kr . (Craig, et al., 1990) These measurements started with 40 liters of water from the Milk River aquifer, Canada, and 70 kg of ice from the Allan Hills region, Antarctica, respectively, and ended with counting the few thousand remaining ^{81}Kr atoms using RIMS.

This was the basis for the method that is being developed further at the Institute for Rare Isotope Measurements (IRIM) of the University of Tennessee under sponsorship from the U.S. Department of Energy (DE-FG05-95ER14497, 12/1/94 - 11/30/99 and DE-FG02-01ER15159, 8/1/01 - 7/31/05) and the National Science Foundation (EAR-9410695, 9/1/94 - 8/31/00 and EAR-0119110, 9/1/01 - 8/31/05). This method consists of a multi-step process starting with (1) collecting the groundwater sample, (2) degassing the water sample, (3) separating Kr from the recovered gases, (4 & 5) two isotopic enrichments reducing interfering isotopes by $>10^9$, and (6) detecting the rare krypton isotope using RIMS in a time-of-flight system. Required water sample size is 20 liters for ^{81}Kr and 10 to 3 liters for ^{85}Kr .

The above few tantalizing results have spurred many other groups to develop alternative analytical methods using a wide variety of ingenious approaches, two of which have resulted in very valuable ^{81}Kr measurements. The first utilized a Cyclotron-based (positive ion) AMS technique developed by Kutchera and colleagues (Collon, et al., 1999) to measure ^{81}Kr in four samples from the Great Artesian Basin, Australia. (Collon, et al., 2000) The second utilizes an isotopically selective spectroscopic method to decelerate only the desired isotope from a beam of metastable krypton atoms that can then be stored in an atom trap and detected by photon burst. This technique, called ATTA, developed by Z-T Lu and colleagues at Argonne National Laboratory (Chen, et al., 1999; Du, et al., 2004) was used to measure ^{81}Kr in water samples from the Nubian Aquifer, Egypt, (Sturchio, et al., 2004) yielding residence times from 200ka to 1Ma. Neither of these methods are as efficient as the RIMS approach, with the Cyclotron AMS requiring processing 16,000 liters of water per measurement, and ATTA 1,000 liters per measurement. Although such large samples are not a serious problem when collecting from a major aquifer, (other than the logistics of degassing such a large quantity of water) it would preclude use for problems where little sample is available, such as from geologic formations having very little water, or age-dating polar ice cores.

So, if it is so difficult to measure ^{81}Kr , why go to the trouble? As the atmosphere is by far the largest reservoir of krypton on earth, with no significant sources (other than the very slow ^{81}Kr production in the upper atmosphere by cosmic rays) or sinks, the concentration of ^{81}Kr should be constant over very long time periods. In addition, no mechanisms for underground production, nor any anthropogenic sources, have been identified (Lehmann et al., 1993). The 50,000 to 1,000,000 year age-dating range of ^{81}Kr is a very good match to studies of very old ground water and polar ice. These can be important for a variety of purposes, such as site-selection of hazardous-waste repositories, assessing basin-scale flow systems, and evaluating long-range climate changes. Finally, it is anticipated that ^{81}Kr “ages” will not require the many corrections that are necessary in the interpretation of ^{36}Cl , $^{234}\text{U}/^{238}\text{U}$ or ^4He ages (Froelich et al., 1991). Analysis of the ^{81}Kr , ^{36}Cl and ^4He measurements from four wells of the Great Artesian Basin, Australia, indicates that ^{81}Kr gives residence times consistent with known hydrogeologic

parameters at all four locations, while only two of the four locations have consistent ^{36}Cl and ^4He results. (Lehmann, et al., 2003) There is clear evidence that subsurface processes are dominating the results at the two aberrant locations. Therefore, hydrogeologists have for many years considered ^{81}Kr a “perfect” tracer for this time interval.

For residence times of less than 50 years, groundwater age-dating is possible by a number of methods, with tritium (^3H) and chlorofluorocarbons (CFCs) having become popular in recent years due to, among other considerations, the availability of sensitive measurement techniques. However, measurements based on these tracers are problematic because of a variety of factors related to either historic variations of their concentration in the atmosphere (^3H), or biogeochemical reactions in the subsurface (CFCs). The emerging $^3\text{H}/^3\text{He}$ method (Torgersen, et al., 1979; Schlosser, et al., 1988) has great advantages over ^3H by factoring out the source function, but there are still limitations because a number of corrections need to be made to the data. (Cook and Solomon, 1997) As a result, hydrogeologic measurements based on these methods contain a lot of uncertainty, unless they are carried out with detailed hydrogeochemical studies utilizing nests of many wells installed at different depths.

Therefore, in the 0.1 to 40 year age-dating range, it is also valuable to have a more practical ^{85}Kr measurement technique, as it has great potential for use in young groundwater studies. It is not affected by many of the factors (declining source concentration, reaction with soil or groundwater, bio-degradation, temperature-dependence) that limit the usefulness of tritium or CFCs. In contrast to tritium, the gradual increase of ^{85}Kr in the atmosphere since 1950, due principally to reprocessing of nuclear fuel, results in a direct relationship between measured Kr-85 concentration and age, (Smethie, et al., 1992) hence a single measurement represents a unique age. Therefore, for the applications discussed above, ^{85}Kr has a substantial advantage over other methods because a reliable, non-ambiguous groundwater “age” can be determined from a single groundwater sample, often taken from an existing well.

Objectives

The overall objective was to complete the development of a RIMS-based analytical technique to determine the concentration of the rare krypton radioisotopes, ^{81}Kr and ^{85}Kr , in samples of interest to the geoscience and planetary science community. Funding was provided by the Geosciences Research Program of the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences at DOE, and the Instrumentation and Facilities Program in the Division of Earth Sciences of the Directorate for Geosciences at NSF.

The capability of determining ^{81}Kr and ^{85}Kr from environmental samples is of interest to both agencies, so the program managers at DOE and NSF decided to “link” the projects. Proposals would be submitted to both agencies, but the project would be funded only if the review process was favorable at both DOE and NSF, thereby assuring sufficient resources for a successful outcome. Although the science applications used to demonstrate the technique in the final project year were different, with DOE sponsoring ^{85}Kr measurements in a young aquifer to elucidate recharge questions and NSF sponsoring ^{81}Kr measurements of very old groundwater, the vast majority of the effort was to be directed towards solving the remaining technical problems, and sponsored by both agencies.

Combining the objectives from both proposals we were to:

- 1) Implement the remaining improvements developed at IRIM to methods for efficient collection of groundwater samples, krypton extraction, isotopic enrichment and RIMS detection to make ^{81}Kr and ^{85}Kr analyses possible at environmental background levels of sufficient accuracy and throughput, enabling these isotopes to become useful tracers.
- 2) Validate the analytical technique by completing measurements of a suite of krypton samples of known ^{85}Kr activity, followed by analyses of groundwater from a hydrogeologically very simple and well-characterized aquifer.
- 3) Apply ^{85}Kr to measuring recharge rates of the Memphis Sand Aquifer, a major aquifer in western Tennessee, test the relative merits of measurements based on single-well and multi-well configurations, and compare with estimates based on conventional physically-based methods, or other environmental tracers such as ^3H and CFCs.
- 4) Demonstrate the practicality of the method by measuring the ^{81}Kr concentration in water from the Great Artesian Aquifer, Australia, for comparison with Cyclotron AMS, but using only 10^{-3} as much sample.
- 5) Disseminate information on ^{81}Kr and ^{85}Kr capabilities and engage the hydrogeology community.

Accomplishments

I. Technique Development:

As was to be expected, most of the effort went into making changes to specific components or operating procedures to the individual steps of the analysis technique, improving reproducibility, accuracy and reliability, and correcting problems identified during the first round of funding. (1994 - 2000) The technique consists of six distinct steps, each of which can operate independently, but all have to work to make a measurement on a sample. We discuss below problems encountered and solutions implemented to each of the steps in the same order that would be followed by an actual sample, realizing that work was not necessarily done in the same order. The six steps are:

1. Collecting a 20 liter groundwater sample without contamination from ambient air.
2. Efficiently stripping all dissolved gases from the sample and transferring it to a metal cylinder for further processing or storage.
3. Separating all other gasses from the one to two microliters of krypton in the sample, collecting it without loss or contamination.
4. Reduction of the interfering major krypton isotopes in sample by a factor of 10^5 , while collecting 50% of the desired ^{81}Kr or ^{85}Kr isotope.
5. Further reduction of the interfering major krypton isotopes in sample by a factor of 10^4 , while collecting 30% to 50% of the desired ^{81}Kr or ^{85}Kr isotope.
6. Counting up to 90% of the remaining analyte (few hundred to few thousand ^{81}Kr or ^{85}Kr atoms) in a RIMS-based time-of-flight (RIS-TOF) mass spectrometer.

Step 1. Groundwater Sampling

As the source of ^{81}Kr and ^{85}Kr in groundwater is from dissolved atmospheric gases, it is imperative that water samples be collected without the possibility of modern air contamination. During a previously funded project, water was collected from a very shallow aquifer by filling evacuated 20 liter glass bottles connected by all-metal valves and 1/8" copper tubing to a miniature inflatable packer that fit inside the 3/8" piezometers. Because the water level in the piezometers was no more than 1 or 2 meters below the surface, sampling was possible using the collection bottle vacuum to pump the water. A flow-control valve prevented premature degassing in the collection tube by keeping the pressure drop below a tenth atmosphere.

For this project, water was to be sampled from much greater depth, therefore in-well pumping was required. To prevent diffusion of atmospheric gasses into the sampling line, the standard PVC line was replaced with much-less permeable Nylon 6, but due to its stiffness, a large-diameter hose and power cable reel was constructed. (See photos on page 31.) The same

sampling bottles from before were used, but a water distribution manifold with a rotating seal, pressure gauge, and regulating valves to maintain positive pressure (preventing premature degassing in the sampling lines) was constructed. Tests of the collection system and sampling bottles over a period of many months resulted in a 0.01 % upper limit to any potential atmospheric contamination.

Standard sample collection protocols must be modified to preclude air contamination. Consider the collection of a tritium sample. Once the well has been purged, water flowing from a pipe at the surface is representative of the formation water, and therefore only needs to be poured into a bottle for transportation to the analysis laboratory. This is not possible in krypton sampling, because even though the water is “old,” it rapidly becomes contaminated by gas exchange with modern air while exposed to the atmosphere.

To prevent mixing of water at the top of the well that is in contact with the atmosphere with water at the screen position, care has to be exercised when inserting the pump into the well. Once the pump is below the water surface, it is started, and only then, slowly lowered, keeping the flow-rate out of the pump to at least the rate water is being displaced by the pump on its way down. This is especially true in a 2” well, where the pump is a tight fit, and can act like a “piston,” forcing surface water downward into the well, and then through the screen into the formation, from which it could take a long time to recover. For example, a 2” well contains about 1 gallon of water in 6 feet, so if the pump were set at a flow rate of 0.5 gal/min, it should be lowered into the well at a rate no faster than 3ft/min. In addition, to avoid collecting water that has recently been in contact with the atmosphere, once in place, the pump flow rate should be low compared to the well production rate, therefore monitoring of water level to prevent significant draw-down is important.

Step 2. Water to Air Separation

Although the water-to-air separator was considered operational at the end of the previous project, it was difficult to obtain consistent results, especially when various parts of the system would freeze, or become too hot, or do numerous other things not in the plan.

A very deliberate and systematic investigation of the degassing process was undertaken to identify the weak links in the system, and conceive appropriate solutions.

To test the system, it was necessary to produce simulated “groundwater” samples with known amounts of dissolved gasses. This was not an easy task! We finally succeeded by filling a large (96 quart) ice chest with tap water, blowing air over the surface, maintaining it at a constant temperature, circulating the water, and allowing it to equilibrate for 3 to 4 days. With 20-20 hindsight, the final configuration resulting from this painful trial-and-error development should have been obvious. With too little airflow, a stagnant water vapor layer on the water surface shields it from the air, resulting low gas dissolution, while too much results in ripples and “excess air” entrapment. If the heater is too small, the high surface temperature of the heating element causes local degassing. (We ended up using a 5 kW, 240 V water heater element with only 40 volts across it.) Too little water circulation results in stratification and poor gas

dissolution, while too much, results in splashing and “excess air.” After equilibration, water was drawn into a 20 liter sampling bottle over a period of ~45 minutes, simulating field conditions.

Consistent degassing of our standard 20 liter “groundwater” samples was achieved by carefully controlling as many of the physical parameters as possible, and strictly following the experimentally derived protocol. Some of the equipment changes can be seen in Figure 1. A helium flow rate controller and totalizer, (upper right) electronic temperature controllers, temperature monitors, and pressure monitors (lower right) make reproducing working procedures possible, and a sample bottle flipper, (upper left) makes handling a full 80 lb sample bottle somewhat easier.

We initially tried to minimize helium usage because very pure (and expensive) gas had to be used to prevent excessive krypton build-up during processing. This makes sense, because, after all, the entire separation process relies on helium sweeping out the tiny amount of analyte (Kr) in the sample, and then very efficiently (in the Kr separator) trapping out any Kr that happens to be in the passing helium stream. Even purchasing 6 9s helium resulted in a krypton blank of ~1 % of the krypton in a typical groundwater sample. Using a LN₂ charcoal trap in the helium supply line, reduces the krypton blank to below our detection limit, even though we are now using considerably cheaper helium, and, more of it. The trap, helium flow controller, and totalizer, have solved many problems and significantly improved reproducibility. Using more helium, but in controlled amounts, allows faster and more complete transfer of water and gasses out of the sampling bottle, and keeps the reservoir water from boiling at the 35 C degassing temperature, a cause of vapor lock in the recirculation system. Using He as the main carrier for the stripped gases, rather than water vapor, eliminates freezing, improves gas transfer from the reservoir to the storage cylinder. Filling to a slightly positive pressure reduces the risk of contamination if a small leak were to develop in the storage cylinder.

A serious problem, discovered just before starting degassing of the ⁸¹Kr samples, required additional changes to operating procedures. The 50 liter reservoir (lower center in Figure 1, with copper tubing wrapped around its upper half) developed a number of small vacuum leaks around the bottom flange. Rewelding only made matters worse. Microscopic inspection showed that corrosion had occurred at the welds, stressing the metal and causing numerous tiny cracks. The only solution was cutting 1” off the bottom, and welding on a new flange. Rather than displacing the degassed water out of the reservoir with air, and trying to dry the reservoir after finishing a batch of samples by blowing heated air through it, which inevitably leaves some moisture behind and fills the tank with oxygen, ideal corrosion conditions, we now push the water out with helium, and overfill it to positive pressure between batches, making conditions less conducive to corrosion. A better choice would have been to make the reservoir from a more corrosion-resistant alloy, such as 316 stainless, rather than the more common 304 stainless.

Step 3. Air to Krypton Separation

The air to krypton separator, shown in Figure 2, operates by utilizing the difference in release time of various species from charcoal-packed columns held at specific temperatures. Manipulating valve positions and trap temperatures at precise time intervals, allows you to vent the undesirable fractions, (Ar, N₂, O₂, etc.) and collect the krypton analyte. As helium flow rate

has significant influence on release time, the helium flow controller, (upper left) and its selectable set-points, (A and B knobs, and A/B switch) has significantly improved timing consistency. Together with the installation of numerous digital pressure monitors, temperature regulators, insulated containers to hold LN₂, 0 C and 95 C baths for all five trap stations, and quick-release brackets at each station so that constant temperature baths can be switched in a few seconds, has resulted in consistent recovery of more than 95 % of the calculated krypton content of the artificially generated “groundwater” standards. The separator has also been tested with simulated air samples containing 0.1 to 10 microliters of krypton, which to the precision of our measurements, showed 100 % recovery.

After carefully developing protocols to consistently recover krypton from artificial “groundwater” samples, almost a dozen real groundwater samples from several shallow aquifers were processed through the water/air and air/krypton separators with no surprises or problems. But, the first sample processed from a very deep well, (660 m) gave us many problems with trap freeze-ups, making a mockery of our carefully developed protocols. In the last step of the separation process, where the separated sample is stored in a “finger” for transfer to the next, instrument, (Figure 2, lower right) the pressure, which usually ranges between 30 and 40 mT, was off scale on our 100 T manometer, a factor of more than 2,500 too high. After some tests, we realized that there was a huge amount of CO₂ in the sample, not surprising, considering that the samples came from a limestone formation. The CO₂ would freeze in the entrance lines to the traps, and when it did get through, would saturate the columns and change the gas release timing. This latter effect, which was a function of the CO₂ load, convinced us that it needed to be removed first. After installing a CO₂ trap, (lower left) and many more runs with artificial “air” samples, this time with large, small, and no CO₂ loads, we were able to develop protocols that worked on all samples, without a-priori knowledge of their composition.

Step 4. First Isotopic Enrichment

The first isotopic enrichment system (Figure 3) consists of a plasma ion source, (far right) velocity filter separator, (brown cube, middle right) and separated isotope collection on 10mm x 7mm aluminized sapphire targets. (far left) This type of ion source produces a 100 nA beam, but requires approximately 2-4 mT of gas pressure to operate. Only 2 % of the gas entering the ion source is ionized, so to keep from wasting most of the sample by pumping it out in a hurry, the entire system is operated in the “static” vacuum mode, i.e., the system is valved off, and getter pumps remove most active gases, leaving the noble gases. Two turbomolecular pumps, operating in tandem, keep the pressure in the mass spectrometer at an acceptable level, while returning most of the neutral krypton to the ion source, giving it another chance to be ionized. Under these operating conditions, it takes about 10 hours for half of the krypton atoms extracted from a 20 l groundwater sample to be processed. The krypton ions are accelerated to 10 keV, sorted according to their velocity, given a slight bend by a thin magnet (middle left) to discriminate against fast neutral atoms, and focused onto a stainless steel baffle with a 2 mm diameter aperture. A slide with 9 sapphire collectors can be positioned behind the aperture. The tenth position is blank, uncovering a faraday cup used to set operating parameters. Two movable faraday cups are set to monitor one of the major krypton isotopes, ⁸⁶Kr or ⁸⁰Kr, while the isotope being enriched, ⁸¹Kr or ⁸⁵Kr, passes through the aperture and is implanted into the aluminum film on the sapphire wafer.

Three significant changes were implemented that improve performance and capabilities. A sample handling manifold (far upper right) with three calibration gas standards and dedicated aliquot valves, 0.1 T and 10 T capacitance manometers, 5 sample “finger” attachment ports, 3 auxiliary ports, and rough and high vacuum bypass pumping ports, was installed. The reservoir volume for each gas standard is 1,000 cc, while the aliquot valve is 0.10 cc, resulting in very slow standard depletion. One delivers 0.1 μl ^{80}Kr (97.1%) per aliquot, the second 0.5 μl ^{86}Kr , (99.6%) and the third is reserved for either a ^{81}Kr or ^{85}Kr standard. In addition to providing isotope dilution calibration of the total amount of krypton, this gas can also be used as a buffer to make the ion source operate at the correct pressure in those instances where not enough krypton was available from the sample.

The most satisfying improvement was installation of the miniature Alcatel ATH+ turbomolecular pump and redesign of the gas recirculation lines, (inset, lower right) which significantly reduced the dead volume in the ion source feed. This reduced the minimum sample size by a factor of two to only 0.8 μl . An unexpected bonus was that we saw considerable less hydrocarbon interference. In a turbo, the motor, bearings, and “O” rings are all in the exhaust path of the pump. Under normal operation, this is not a problem, as any hydrocarbon vapors are simply exhausted. But in our application, these gases feed right back into the ion source, resulting in hydride formation. And as $^{84}\text{KrH}^+$ has the same q/m as $^{85}\text{Kr}^+$, the hydride peak is the limiting factor in enrichment performance, irrespective of how small the mass profile tails are in the adjacent mass channels. We have experimented with many different types of traps to reduce hydride production. Two sequential traps seem to work best. The first is filled with a proprietary (Balzers) CuO coated zeolite at 400 C and converts larger hydrocarbons to simple molecules, such as H_2 , CO and CO_2 . The second is filled with SAES St 707 pellets at room temperature, which getters the H_2 , CO and CO_2 coming from the first trap. Both traps are made from 1” pieces of $\frac{3}{4}$ ” stainless tubing, thereby not increasing source volume by much. Because the hydrocarbon emission from the 50 l/s Balzers pump improved slowly over the years as parts outgassed, with the smaller motor, bearings, and fewer “O” rings, we expect the Alcatel pump to clean-up much faster.

Pressure leak-down measurements of the ion source were a factor of two to four faster than calculated from the dimensions of the ion extraction canal. The present source uses quartz components that have no positive mechanism to seal the gas inlet, electrode inlet, and anode. A new, more robust design was completed, and all quartz components have been delivered. The new ion source assembly will be installed when it becomes necessary to replace the present source filament. We anticipate this change to further reduce sample size to the theoretical limit set by the number of ^{81}Kr and ^{85}Kr atoms in the sample, and also, improve mass peak shape because of less scattering because of the smaller gas load.

Realizing that if for every ^{81}Kr measurement, there is also available a ^{85}Kr measurement, significantly more can be learned. This could set limits to, and make corrections for sample contamination by modern air, and also provide a better understanding of, and correct for, mixing from different water sources within the aquifer. This would require simultaneous collection of ^{81}Kr and ^{85}Kr during isotopic enrichment. We have completed a conceptual design, and located a supplier of enriched ^{83}Kr calibration gas that is willing (for a price!) to further enrich it, making the potential of contamination in the ^{81}Kr and ^{85}Kr mass channels negligible.

Step 5. Second Isotopic Enrichment

The Second Enrichment System's quadrupole filter assembly, which had been damaged and repaired many times over the years, was replaced, bringing performance back to specifications. Experimental determination of losses and memory effects from implantation into the pole rods as a function of tuning and pole temperature confirmed earlier measurements that improvement (less loss and memory) at higher temperatures was possible. But, as the performance of a quadrupole filter (throughput, abundance sensitivity and efficiency) depends critically on the geometry, (at sub-micrometer tolerances) a new set of poles was fabricated with dimensions calculated for operation at 400 C. These, together with an internal (to each pole) heating system, were installed. When tested, the internally heated poles showed the best quadrupole operation at 350 C, not too far from our calculated target, which when coupled with the ability to raise the pole temperature to 500 C during pump-out between samples, totally eliminated the memory effects that had been plaguing us for years. An added benefit of temperature-regulated quadrupole internal components, coupled with thermal control of the pole-driving electronics, resulted in significantly improved system tuning stability. Although sample loss to the poles during enrichments was reduced from ~50% to ~35%, (not the hoped for 10%) this loss was still significant, and its variability resulted in considerably reduced accuracy. We clearly had taken the heated pole solution as far as it could go.

For practical isotopic enrichment, throughput must be high, requiring acceptance of ions of high longitudinal and transverse energy. Transmission of these ions without striking the poles (the loss mechanism) scales as the RF frequency squared, while the RF power required to transmit an ion of a particular mass scales as the fifth power of the frequency. Tests at mass 40 (Ar) showed that even a modest frequency increase from 2.40 to 2.65 MHz resulted in a significant performance improvement, encouraging us that raising the operating frequency from 2.4 to 3.1 MHz would result not only in reduced sample losses, but also in improved enrichment factor. The quadrupole manufacturer's best and newest driver electronics only went to 300 W, not much higher than the 200 W limit of our old system. (Plus it cost ~10K) So the solution was to purchase a linear amplifier and simply boost the output of our quadrupole control system. Modern communications equipment is now all geared for much higher frequencies, and the only suppliers for the frequencies we needed were for medical applications, which now cost even more than military applications. We tried purchasing an amateur radio linear amplifier, but one had to have a license, (which none of us had) but worst still, their equipment is only designed for short (5 min) duty cycle, and would quickly burn up in our application. We finally found a very nice 1,500 W surplus Merchant Marine linear amplifier on E-Bay for \$750.00, and the required HV power supply (also on E-Bay) for ~\$1,000.00, but just as it was all coming together, our undergraduate student, who was quite good in electronics, decided to leave physics, and go to another school. With so many other things needing our attention at IRIM, this fix, which probably would have worked, ended up being pushed to the back burner.

Some of the components discussed above can be seen in Figure 4. Starting on the right panel, inset, upper right, three aluminized sapphire sample collectors from the first enrichment system are shown. The rightmost one carries the sample as individual atoms buried about 6 nm in the Al, the middle one has been marked to indicate the implant centroid, while the one on the left was zapped by a laser (under vacuum in the sample lock) to evaporate the Al and release the krypton atoms. To the upper left can be seen one of the fans on the pole-driver interface that

regulate the temperature. In the middle is a panel with the pole and pole casing temperature controllers, with the associated heater power supplies mounted behind the aluminum plate. At the bottom is the HV power supply for the linear amplifier. On the left panel is the quadrupole MS system electronics rack. In the middle of the rack, in warm cream colors, is the marine transmitter linear amplifier. Above and below it, in bluish gray colors, are the original quadrupole control electronics, which now become the driver for the linear amplifier. The important point (although not tested) is that the entire system, including the linear amplifier, is inside the quadrupole control system feedback loop, so only the power is upped by a factor of 10, but all other functions stay the same.

Step 6. RIMS detection of ^{81}Kr or ^{85}Kr

Many changes were made to the krypton TOF mass spectrometer, Figure 5, all of which solved real problems, but the MAIN problem, high blank, is still with us. An intermittent leak in the feedthroughs of the primary TOF mounting flange was repaired by grinding and rewelding, so that complex component did not need to be rebuilt. The pumping system of the RIS-TOF mass spectrometer was reconfigured with expansion joints and more rigid mountings at key locations to eliminate thermal stresses during baking. The calibration gas reservoir, aliquot valves and expansion volume were mounted vertically on a massive custom adaptor going straight into the TOF detector cube, eliminating another stress point and occasional leak source. New UHV valves with different sealing mechanism (from VAT) to reduce krypton “squeeze-out” upon sealing (a minor blank contributor, considering our present problem) were installed, solving another minor leak between the sample lock and the TOF. The pressure now returns to typically 1.5×10^{-10} T after repeated bakings with no sign of leaks.

At the beginning of this funding cycle, major servicing was performed by Continuum on the main Nd:YAG pump laser and associated dye lasers, bringing them back to spec operation. Unfortunately, when the laser jocks leave, they only care that their equipment meets specs, but have no concern in what direction the output beams now go. So, it takes us at least another two weeks to get everything else realigned. In January 2002, major servicing was again done by Continuum on the primary Nd:YAG pump laser and associated dye lasers, replacing several key components, including the Pockels Cell. The Pockels Cell, replaced in January, failed again in December 2002. Considerable time and effort was lost, both in having to repeat twice the alignment of all down-stream optics, but also in working with the Pockels Cell manufacturer for a more permanent solution. This time, we worked directly with the manufacturer, bypassing Continuum, who now didn't repair it to Continuum's specs, but instead used a more robust design. We have had no more problems with this component. The output at all of the wavelengths required for Kr RIS was better than ever before, but then caused laser damage to the final beam combining optic going to the mass spectrometer. Considerably higher damage threshold optics are now available, so it was replaced and have had no more problems. A final laser difficulty, mode-hopping in our third dye laser, which lead to wavelength jumps and large RIS signal fluctuations, was finally solved by replacing it with a third dye laser, similar to our other Continuum dye lasers, but older. As this required a major optical reconfiguration, we fixed some other problems with the laser system that had been frustrating us, and are shown in Figure 6.

We have had some laser problems, and some vacuum problems, but on the whole, the RIMS system has not been fickle. All the careful redesign and assembly of optical lay-out and vacuum system components, with special attention to stability, have been worth while. It is now possible to start the system up after having it on stand-by for many months, and it will still be aligned so that you can see a RIMS signal within a short time period, and only minor alignment is required to get back to full sensitivity.

So why are we frustrated? Fifteen years ago, this same system, with a much weaker and flaky laser system, demonstrated a 100 atom, 3σ ^{85}Kr detection limit in 10 minutes analysis time with 90% of the atoms in the sample counted. (Thonnard, et al., 1992) At that time, it took a very good laser physicist (not the PI) a month of careful tweaking to fleetingly have the present sensitivity. Today, (actually, 18 months ago) after turning the system on, within a few hours of adjustments, this sensitivity is routine, but measurements cannot be carried out because of the very high blank. At the time of the above publication, the ^{84}Kr in-growth (blank) was frequently not measurable, i.e., after 10 minutes waiting with the vacuum system valved off, we'd see no change in signal, and just from the signal fluctuations, would assign an upper limit of 1,000 ^{84}Kr atoms min^{-1} . At IRIM, this same measurement has resulted in numbers ranging from 80,000 to 160,000 ^{84}Kr atoms min^{-1} . We purchased a 5% Kr in Ar tank, used the RIS-TOF system as the world's most sensitive leak detector, found a few small leaks, fixed them, retested, and could not see any significant change in the blank. Tantalizingly, during the last two weeks of Dr. Stone's post-doc at IRIM, and after funding ran out on this project, some hints were seen that there are several internal leaks between the VUV 4-wave mixing cell and the TOF and the VUV detection cell and the TOF. This could explain a lot of observations, but a clear solution is not apparent at this time, because of loss of technical expertise when skilled individuals in niche fields retire.

II. Measurement Validation

The present (mid-2007) atmospheric ^{85}Kr activity is 75 dpm/cc Kr. We have on hand at IRIM the following calibrated ^{85}Kr standards that can be used for activity calibration, sensitivity determination, saturation assessment, memory assessment, and blank assessment.

<u>Quantity (cc)</u>	<u>Activity (1/1/08)</u>	<u>Fraction of Atmospheric</u>
4.5	400	5.33
5.0	40.0	0.53
10	19.5	0.26
20,000	7.96	0.11
2.6	0.00	0.00 (pre-bomb)

These would be ideal samples to process in the first enrichment system, second enrichment system, and the RIMS TOF system. Measurements of these would assure us of the analytical method's reproducibility and reliability. Because of the current reproducibility and variable sample utilization problems with the quadrupole second enrichment system, and the RIMS system blank, it would not have been useful to process these now.

We also have on hand 15 groundwater samples collected in September 1997 from the University of Waterloo's test site near Sturgeon Falls, Ontario, Canada. Samples were collected from a nest of piezometers along a gentle flow divide ranging in depth from 1.5 m to 25 m. This site has been well-characterized by many methods, and consists of a very uniform clayey fine-grained sand having a recharge rate of less than 1 m/a. This provides a good test in a simple hydrological setting. Krypton activities are expected to range from 35 to 2 dpm/cc. About half of the samples have been degassed and the krypton stripped out. Processing of these will resume after analytical validation has been demonstrated.

III. Showcase ^{85}Kr Application

IRIM participated in a large AwwaRF funded study of recharge to the Memphis aquifer in Shelby County. (Gentry, et al., 2006) Two nests of sampling wells were installed to depths ranging from 35 ft to 160 ft, starting in the surficial aquifer, and ending several 10s of feet inside of the Memphis Sand. (Figure 7, page 29) One nest was installed in a window of the clay confining unit, and the other, ~2,000 ft down gradient from the window in a confined region having a ~50 ft thick clay cap. Two existing wells were also sampled, one ~2,500 ft SW and the other ~3,600 ft NW from the confined nest. A wide range of hydraulic tests were run, including pump tests and slug tests, and samples were collected for a complete suite of water chemistry, tritium, $^3\text{H}/^4\text{He}$ and ^{85}Kr analyses. Three major sampling campaigns were undertaken, covering both dry and wet seasons. We had hoped to complete the analyses before the project was finished, so that the comparison to the other methods could have been included in the report. Sixteen 20 l groundwater samples were taken for ^{85}Kr analysis, Figure 7, pages 30 and 31. Seven of these have already been degassed and are stored in hermetic aluminum cylinders under slightly positive He pressure, while the rest are stored in their original glass sampling containers. It will be very valuable to compare ^{85}Kr results with the other analytical methods.

IV. Showcase ^{81}Kr Application

In January 2003, Dr. Bernard Lavielle from the CNRS and the University of Bordeaux, France, visited IRIM to see our rare krypton isotope measurement facility. He had received funding from ANDRA, the government agency charged with managing radioactive waste in France. (Lavastre, et al., 2004) ANDRA was in the process of developing an underground research laboratory in Meuse/Haute-Marne, northeastern France, to test numerous aspects of long-term retrievable radioactive waste storage. They were in the process of sinking a 10 m dia. shaft through 120 m of surface rock, 300 m of very dense Oxfordian limestone, followed by 70 m into a very uniform, bone-dry, 130 m thick clay layer. At the 490 m depth, many side-shafts will be drilled to accommodate a variety of laboratories to study long-term confinement issues. At 550 m depth, the clay ends and you enter into a second very dense, Dogger limestone. The ANDRA hydrologists wanted to have ^{81}Kr analyses from water seeping out of the limestone walls as the main shaft was being sunk, and from three off-site well nests, one 7.4 km to the SE, one 9.3 km to the E and one 11 km to the NE of the main shaft. These test wells went to depths of up to 900 m, sampling from both the Oxfordian and Dogger limestones. Part of the hurry was

because French law gives only 12 month permits for geologic testing wells, and by the end of February, 2004, they all (20 Million Euros!) had to be filled with concrete.

Dr. Lavielle wanted to learn how to set-up the sample collection, degassing and Kr separation, enrichments, and RIMS TOF system. He had a Post-Doc that could spend three months in early 2004 at IRIM to help us with the analyses. As ANDRA was really serious of having ^{81}Kr results by the end of the year, the PI tried to send Dr. Lavielle to Dr. Lu's group at Argonne to make the measurements with ATTA. ANDRA was so concerned about the low productivity of the wells that they barely agreed to 20 l per well; even 50 l was "impossible" by their assessment. So this is a clear example where the RIMS efficiency is curtail. We sent six IRIM sampling bottles to Bordeaux, the PI joined the bottles in late September 2003, and we went water collecting. (Figure 8.) Lavielle's Post-Doc spent three months with us in early 2004, and all samples have been degassed and Kr separated. (Lavielle, et al., 2005) Now, if only everything else were working at IRIM, we'd be done.

V. Information Dissemination

At the moment, we feel somewhat reluctant to further expound on how to measure ^{81}Kr and ^{85}Kr , since we are still trying to figure that out ourselves. Clearly, enough people have become excited about the possibility, as several are in the process of developing alternative analysis methods, and others are interested in using these radioisotopes. We've had more than a dozen unsolicited e-mails asking about having ^{81}Kr and/or ^{85}Kr measurements made. At this point, it would be nice to simply finish the samples we collected and started processing.

Discussion

Although we were unable to meet our primary goal of making the RIMS-based analytical system for ^{81}Kr and ^{85}Kr measurements functional as an analytical tool, much was learned and valuable infrastructure set-up. IRIM is the only facility with the potential capability of measuring these two isotopes that has all aspects of the process, from sampling to final analysis, integrated together at one location. Care has been taken for efficient and contamination-free handling of samples so that it would be possible to reach the theoretical limit in sample-size set by the number of analyte atoms in the original sample. Efficiency is not very important for the first "demonstration" measurements of a new technique, which can be accomplished with very large samples from carefully selected sites. But for a system to be practical and used routinely in a variety of applications, it needs to be useable without a huge investment in sample collection and processing. In many circumstances, there is simply not enough sample available to count only 0.01% to 0.1% of the analyte atoms, which is the efficiency demonstrated by the two newer analytical methods

The failure in achieving our goal was primarily due to two weak links in our long analysis chain. The first is fundamental - the quadrupole-based second isotopic enrichment system is not viable due to the physics of its operation. The PI has been aware of this for more than 15 years, but has been unsuccessful in obtaining funding to replace it. Too many resources have been lost

in endless attempts to make it work “just a little better” so that a “few additional measurements” would convince sponsors that the method would succeed in the end.

The second weak link - the RIMS system - was not really a weak link, but a severe case of bad luck. We achieved excellent sensitivity, stability, and reliability, but failed to pin down the source of the high krypton blank before running out of resources. We went down many blind alleys, but it now appears to have been due to several internal leaks in defective MgF₂ windows between the TOF and its wavelength-conversion gas cells.

Both problems are solvable. The first would require a significant investment for a custom static mass spectrometer. The second, only some operating funds and a modest supply budget.

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Participants

Directly Involved in Project

Norbert Thonnard, PhD - Principal Investigator

Sets the overall direction of the project, prioritizes effort to achieve the ultimate goals, trains the individuals involved, and manages the financial resources. In addition, the PI is intimately involved in all of the sub-components (hardware and operations) of the analytical instrumentation, and leads and executes the design and construction thereof.

Larry D. McKay, PhD - Co-Investigator

Oversees the application of this emerging methodology to hydrogeology. He reviews plans for sub-system development and operational procedures to assure that reliable and relevant data to the scientific questions being addressed will be forthcoming. He prioritizes the type of hydrology problems to investigate to best demonstrate the utility of the methodology.

Ronald E. Yoder, PhD - Co-Investigator

Was originally going to participate during the last year of the project in application of ^{85}Kr to understanding recharge in the outcrop region of the Memphis Aquifer, where he had previously identified significant heterogeneity in the overlying soils. Unfortunately, due to delays and difficulties in implementing the ^{85}Kr methodology, this part of the project could not be started.

Kathy O. Stone, PhD - Research Associate

Dr. Stone, once having received her Ph.D., rejoined us as a Research Associate in November 2002. From 1995 through 2000, as a Graduate Research Assistant, she was a major participant, concentrating on the RIMS system. Presently, in addition to having full responsibility for the RIMS system, has participated in field work collecting samples, and worked with the sample degassing and krypton separation systems.

Charles F. Joyner - Senior Technician

Except for the PI, Mr. Joyner has the widest experience base with the analytical technique being developed here. During this project, Mr. Joyner did almost all of the experimental work on both enrichment systems, both operation and data taking, and executed the improvements to the systems. In addition, he has repaired and maintained various electronic and mechanical systems as the need arose.

Nick Moore - Undergraduate Research Assistant

Mr. Moore joined this project in March 2002. He has learned operating and maintenance procedures on our vacuum systems, and has constructed various components for our gas calibration system. Due to his heavy class load, his participation had to stop during the fall 2002 semester.

David Gains - Undergraduate Research Assistant

From summer 2003 to summer 2004, Mr. Gains worked with the PI in designing, and then constructed various analog and digital electronic components for our laboratory. This included flow controllers and flow integrators for the degassing and Kr separation modules, and adaptation of a surplus marine radio transmitter to improve the operation of a quadrupole mass spectrometer.

Scott Scarborough - Senior Technician

Mr. Scarborough, a senior-level technician, was employed at our laboratory from mid-August 2003 through the end of October 2003. Although highly experienced, his skills were not as compatible with our needs as anticipated, therefore left before making significant contributions.

Randy Gentry, PhD - Associate Professor at the University of Tennessee, Knoxville

Is PI on the MLG&W/AWWRF sponsored project, on which the PI of this NSF project is a Co-I, and directs the selection and sampling of water from the Memphis Aquifer for Kr-85 analysis.

Bernard Lavielle, PhD - CNAB and the University of Bordeaux, France

Is collaborating in obtaining water samples from a proposed nuclear waste repository site in France for Kr-81 analysis and in developing a RIMS-based Kr-81 analysis system for his laboratory.

Veronique Lavastre, PhD - Research Associate at CNAB, France

Is responsible for understanding and interpreting the geologic setting of the sampling site and the collection of samples for Kr-81 analysis from the proposed French nuclear waste repository site. Worked for three months with us in our laboratory adapting Kr separation techniques to the unique composition of deep groundwater samples and participated in processing samples. Became familiar with our analysis method for implementation in their own laboratory at the University of Bordeaux.

Collaborators

Jamie Gilmour, PhD, - Department of Earth Sciences, Manchester University, spent a 15-month sabbatical at IRIM and participated in all aspects of RIMS analysis development, and in studies of meteorites. In addition, he served on Dr. Stone's Ph.D. committee.

Typhoon Lee, PhD, - Institute of Astronomy and Astrophysics, and Institute of Earth Sciences, Academia Sinica, Taiwan, works with the PI in developing ultra-sensitive instrumentation for element and isotopic analyses of sub-micrometer sized dust returned by the Stardust comet fly-by space mission.

Charles Hohenberg, PhD, - Department of Physics, Washington University, participates in applications of Kr and Xe isotope measurements of extraterrestrial samples.

Organizational Partners

Academia Sinica, IES, Taiwan

Has provided funds for development of new hardware by IRIM for the comet dust analysis system at IES, opened their facilities to mutual research projects, and facilitated collaboration by their personnel with us.

Memphis Gas, Light and Water, and AwwaRF

Has provided funding for groundwater collection and analysis of ^{85}Kr therein, and given on-site support for access to their extensive well-field.

University of Bordeaux and CNRS, France

Has provided funding in partial support of groundwater sampling and ^{81}Kr analysis, travel support for the PI to visit their facilities, and supported a research associate at IRIM for a three-month, in-depth collaboration.

Contributions

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Web/Internet Site URL:

<http://web.utk.edu/~irim>

Training and Development:

The wide variety of experimental skills required to accomplish the goals of this project provide many opportunities in learning both hands-on laboratory methods and 'arts,' and a deeper understanding of the science problems that can be solved with emerging analytical techniques. This learning experience is applicable to all participants in this project, be they technical assistant, undergraduate or graduate student, research associate, visiting scholar, professional colleague, or the PI. Technical skills developed include, but are not limited to:

- (1) Vacuum system design principles, operation and maintenance;
- (2) collection of ground water samples for trace gas analysis and general sample handling and documentation;
- (3) separation of air from water and noble gases from air without contamination and sample losses;
- (4) principles and operation of various types of mass spectrometers, including quadrupole, ExB velocity filter and time-of-flight;
- (5) laser system safety and proper handling of optics,
- (6) building of simple electronic sub-assemblies, and trouble-shooting electronic instruments;
- (7) making of various mechanical fixtures and use of shop tools;
- (8) data taking and analysis, and learning to judge the quality and reliability of what has been observed; and
- (9) many other practical skills too numerous to mention.

Outreach Activities:

Presentation entitled "Practical Applications of Atomic Physics: Solving Problems Ranging from Pre-Solar System Nucleosynthesis to Age-Dating Polar Ice" to the students and faculty of the Department of Physics, East Tennessee State University, Johnson City, TN, November 12, 2001. Judged Science Fair projects presented by first through fifth grade students at Midtown Elementary School, TN, April 24, 2003, and May 13, 2004.

Contributions within Discipline:

The primary aim was to improve, to the point of being practical, a new analytical technique that should enable analysis of promising stable and radioactive noble gas isotopes for studies in the geosciences. The high sample utilization efficiency of the analytical technique under development would have enabled measurements of limited-sized samples, such as the Kr-81 concentration in water extracted from underground formations in arid regions to assess isolation time-frame from the environment if used for waste disposal, or the Kr-81 concentration in deep polar ice cores to age-date them in long-term global climate change studies. Although a few

earlier measurements were successful, technical difficulties in the course of this project, which in principle should be surmountable, prevented us from reaching our goal within the available budget and time. At this point, our most important contribution within the discipline has been to spur others to develop alternative analytical techniques for these rare, but valuable isotopes.

Contributions to Other Disciplines:

The RIMS mass spectrometer being developed as part of the instrumentation required to meet the primary mission goals would be an ideal instrument for Kr and Xe analyses in the planetary sciences. The small sample capability and high sample utilization efficiency would be particularly valuable for analyses of samples returned by robot space probes. Fewer technical difficulties need solving for this application compared to measurements of environmental Kr-81 or Kr-85, so modest additional resources could make this application practical.

Contributions to Human Resource Development:

Since the start of this project, three students and a research associate from the Institute of Earth Sciences at the Academia Sinica, Taipei, have been involved in various aspects of the research. Some of the research opportunities and practical skills they were exposed to are listed in a previous section entitled “Training and Development.”

Contributions to Resources for Research and Education:

Although not completed, the analytical facility being developed is unique, and has already generated many opportunities for collaboration between researchers at institutions world-wide.

Contributions Beyond Science and Engineering:

The development of the proposed analytical method was not completed, but when measurements finally become successful, either by this method, or other approaches, will provide better data for assessing global climate changes by dating polar ice in the 50k to 1M year time period using Kr-81, assist in the selection of hazardous waste repositories by assuring long groundwater residence times using Kr-81, and provide new means for ground water resource management by studying aquifer recharge, identifying potential pollution pathways and assessing groundwater flow patterns using Kr-85.

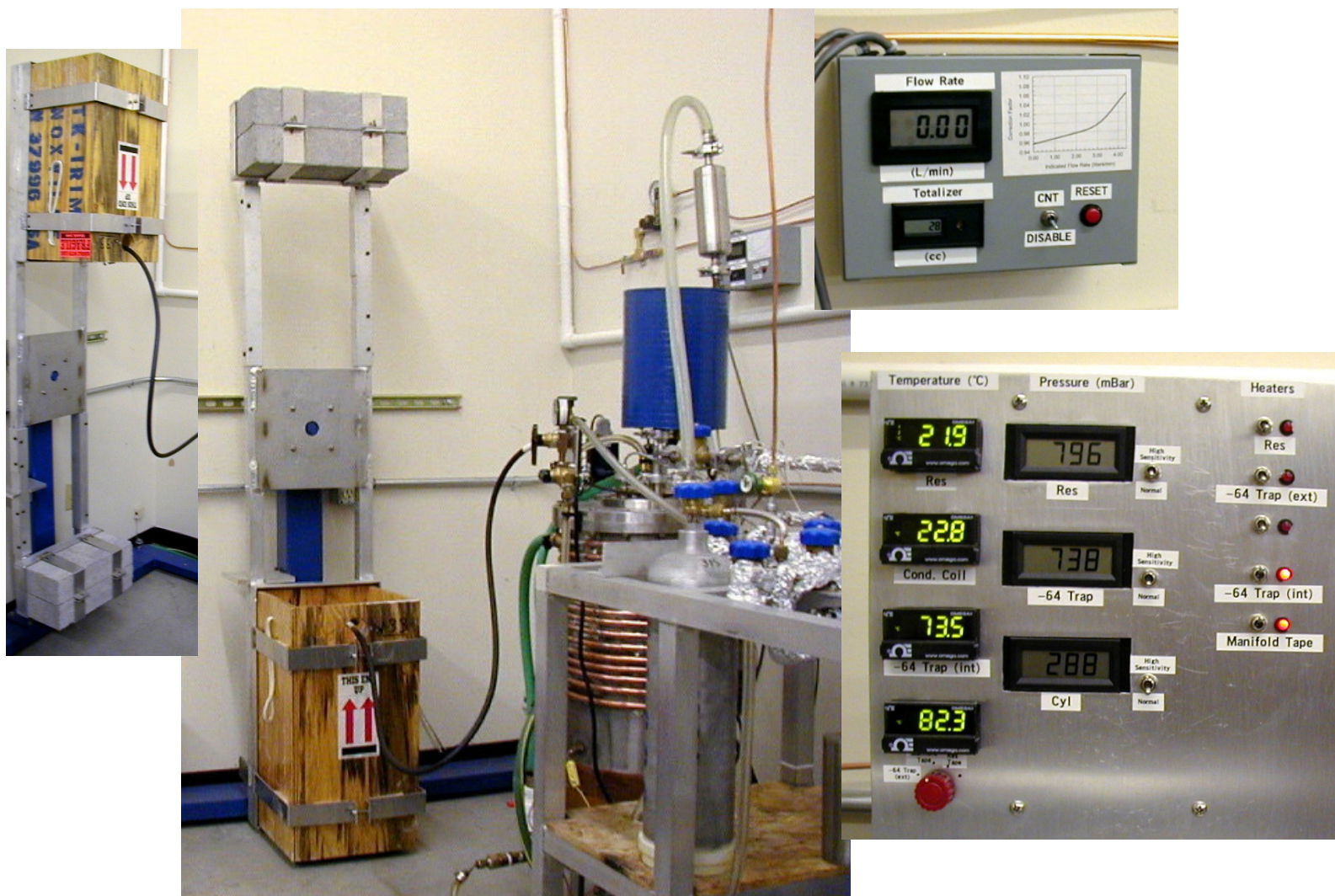


Figure 1. Water to Air Separator

Gases from headspace and water are transferred to evacuated reservoir, (center) circulated and sprayed in low pressure He atmosphere, and pumped into Al cylinder. (foreground) Bottle flipper, (clockwise from left) He flow controller and totalizer, and trap temperature controllers have resulted in efficient and consistent operation.

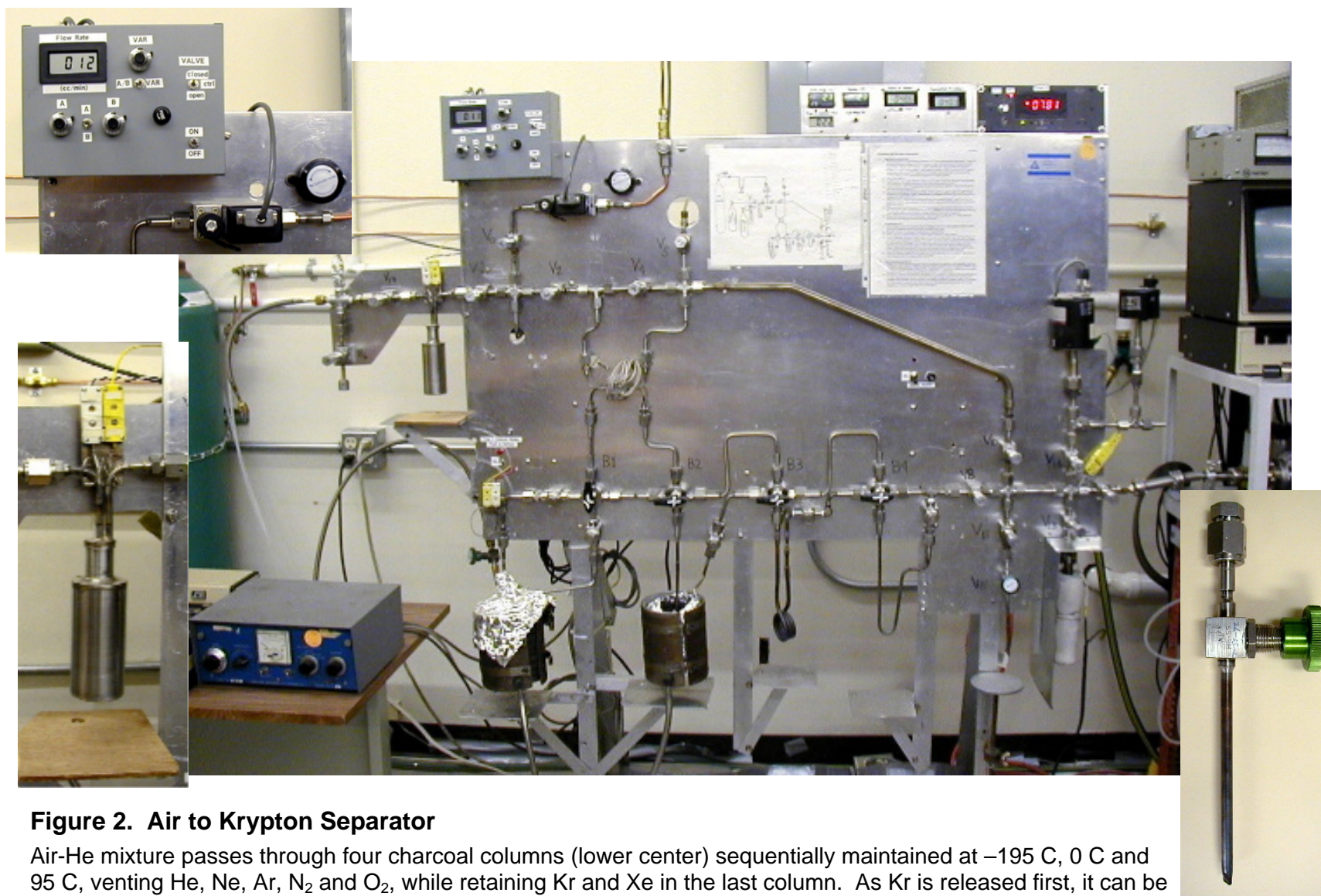


Figure 2. Air to Krypton Separator

Air-He mixture passes through four charcoal columns (lower center) sequentially maintained at -195°C , 0°C and 95°C , venting He, Ne, Ar, N_2 and O_2 , while retaining Kr and Xe in the last column. As Kr is released first, it can be collected in the small finger (lower right) without Xe contamination. A Ti getter at 890°C removes residual molecular contaminants. Temperature regulated trap (lower left) freezes out CO_2 before it enters the columns. He flow controller, (upper left) back-pressure regulator, multiple temperature regulators, pressure monitors, and quick-release constant-temperature bath brackets have resulted in consistent Kr recovery.

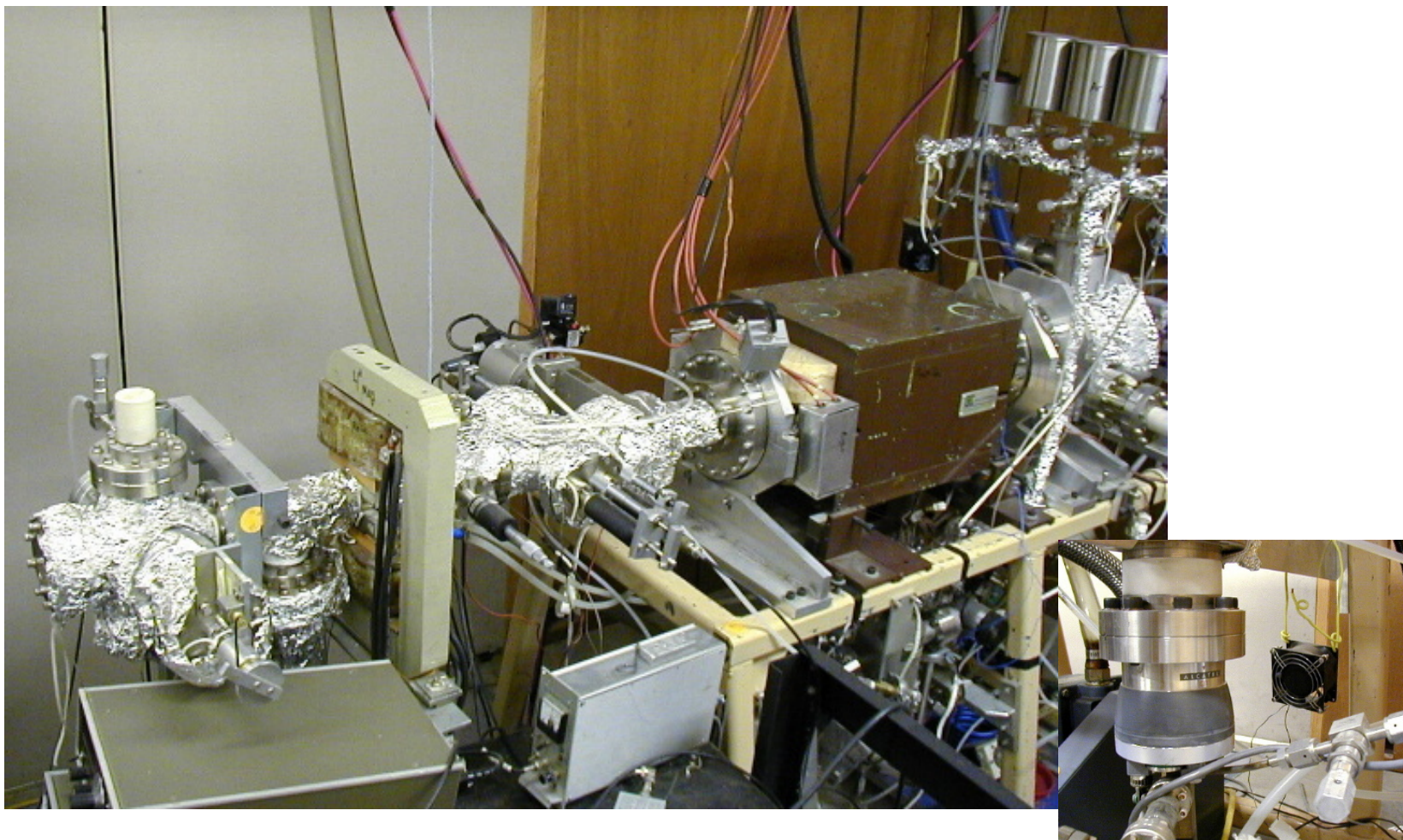


Figure 3. First Isotopic Enrichment

Sample fingers are connected to calibration manifold (upper right) having low-pressure absolute manometers and Kr-80 and Kr-86 gas available for quantitation. The sample is released to mass spectrometer and compressed to source with tandem turbo pumps, the second one being of very small volume (lower right) resulting in 0.0008 cc Kr minimum sample, ionized, accelerated to 10 kV, separated by a velocity filter, and implanted in an aluminized sapphire target (left) for transport to the next stage.

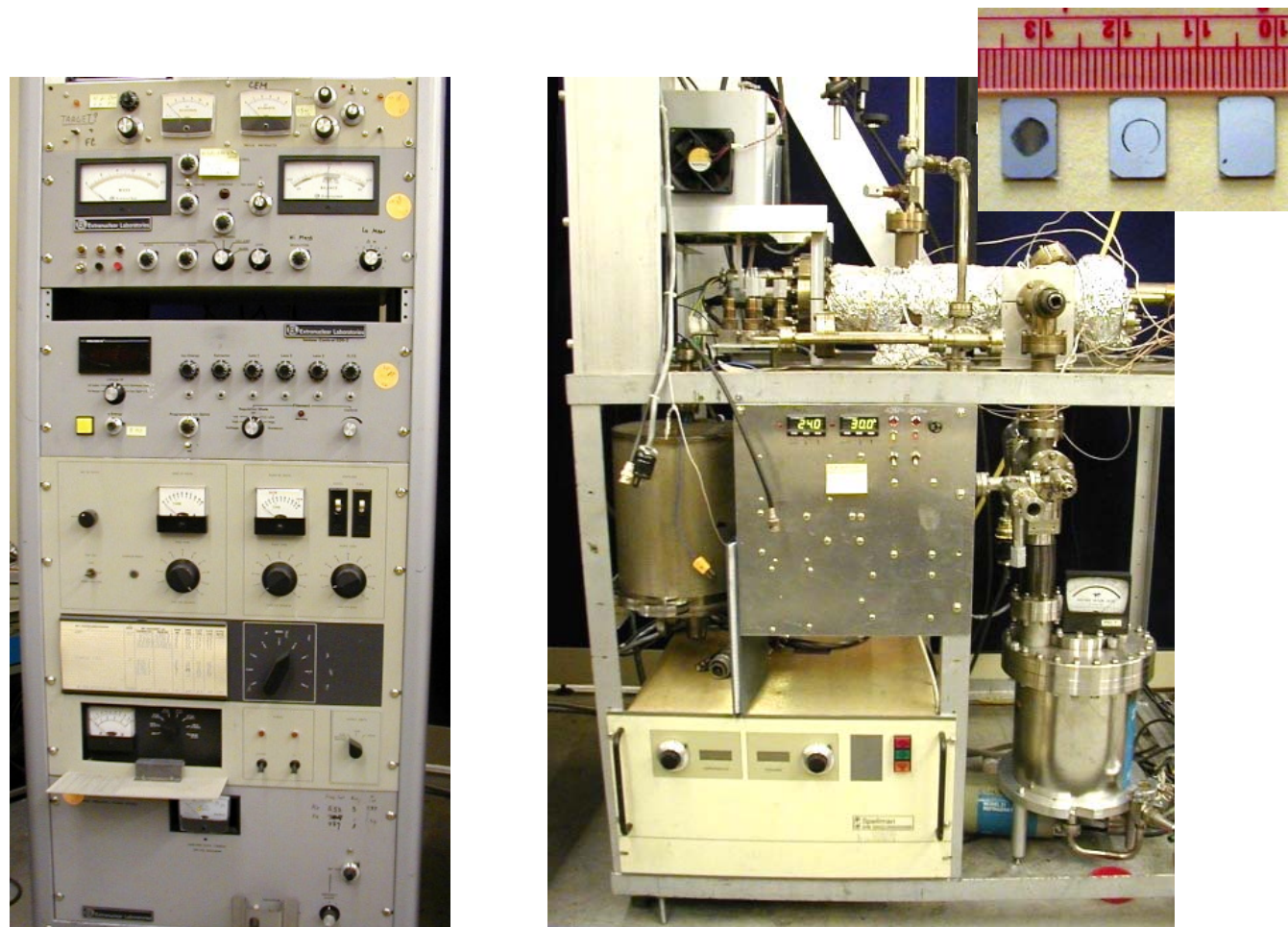


Figure 4. Second Isotopic Enrichment

After loading into vacuum lock, enriched sample (upper right, inset with cm scale) is released by laser evaporation of aluminum. Quadrupole mass spectrometer casing and rods are regulated to 350 C, and can be raised to 500 C between samples, (right center) reducing memory. Linear RF amplifier (left center, marine surplus) increases the spectrometer RF power from 150 W to 1.5 kW, permitting operation at twice the frequency. This should increase transmission and isotopic selectivity, while reducing stray Kr ion flux to the poles.

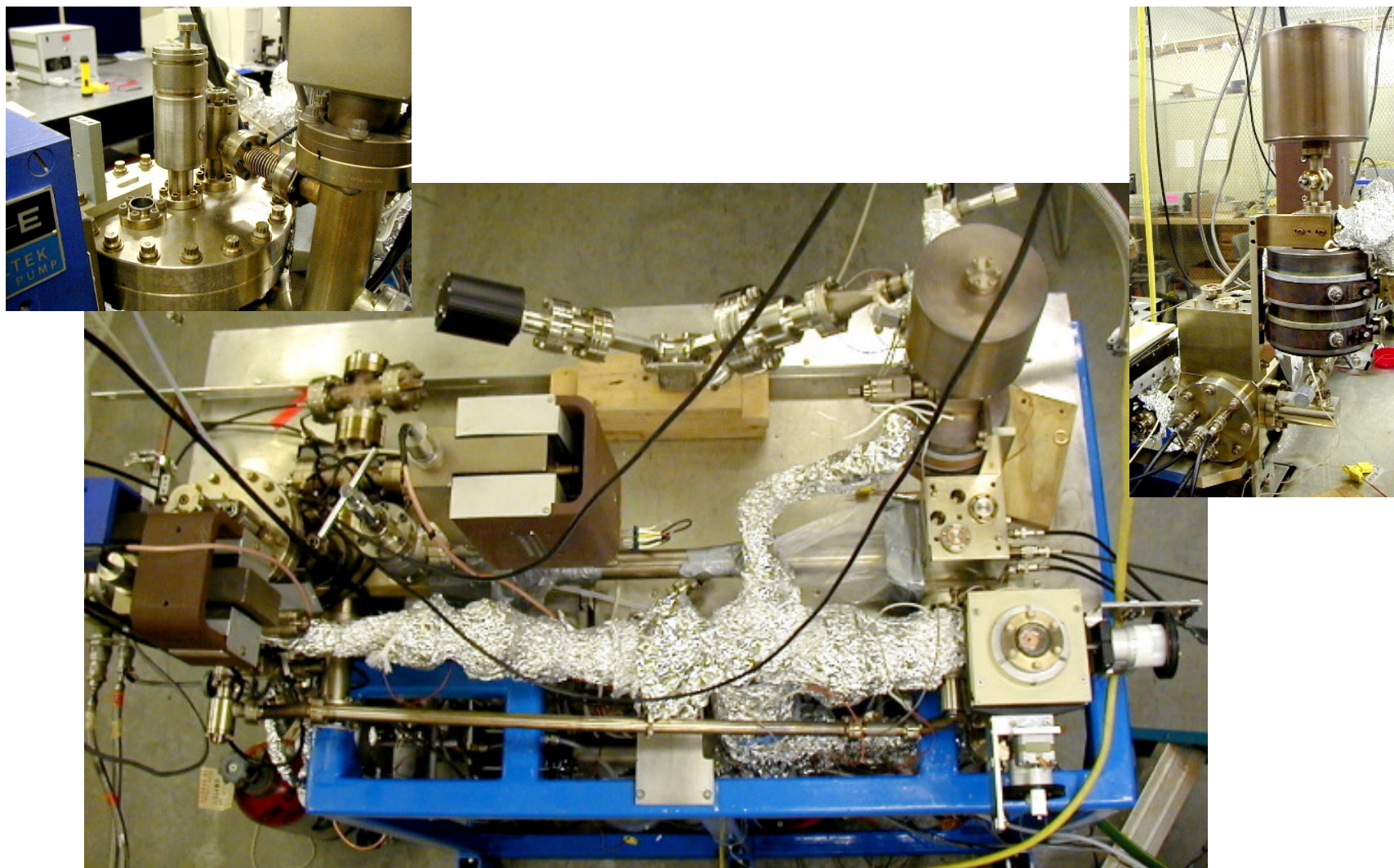


Figure 5. Krypton TOF Mass Spectrometer

Ion flight path is from left to right. Most changes were implemented to reduce thermal and mechanical stresses during baking to eliminate leaks. The entire pumping manifold (wrapped in Al foil, lower center) floats on a central bracket and is only connected by bellows to the instrument. The sample lock (upper left) and main ion pump (center) have new valves to reduce Kr squeeze-out during closing, and the calibration volumes and aliquot valves (upper right) are mounted vertically. Heavy components have been repositioned to balance torques about the main support axis.

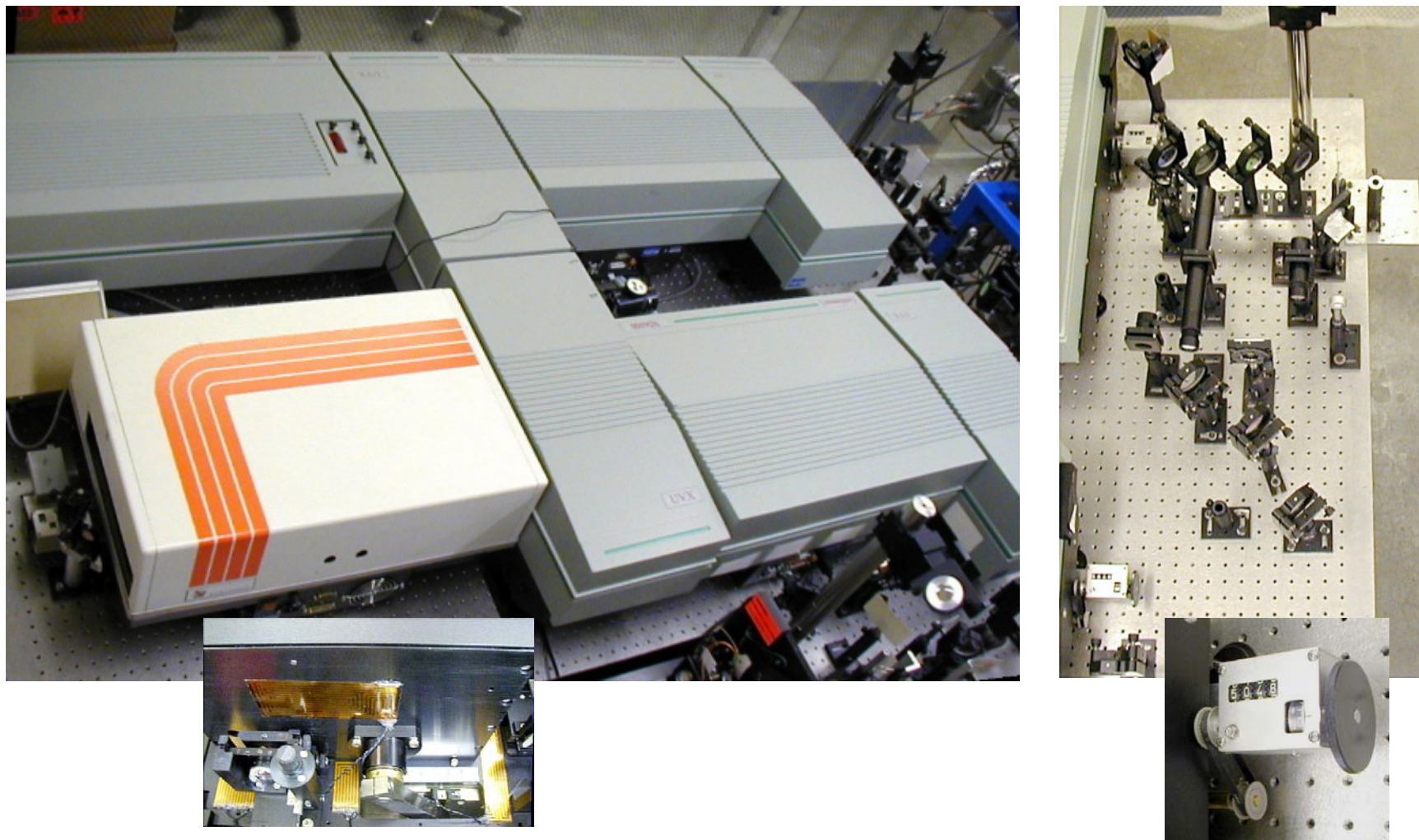


Figure 6. Kr RIS Laser System

A third dye laser (orange/white rectangle) was added to reduce signal instabilities due to mode-hopping. Redesigned telescopes (upper right) have improved laser beam quality and overlap. Mechanical wavelength drives (lower right) ended frustration with wavelength calibration jumps, while temperature stabilization (lower left) reduced wavelength drift.



Figure 7. Shelby Farms Sampling

Studying recharge through windows in confining unit. Clockwise from upper left: Rotosonic drill-rig in place, drilling, collecting core sample, clay confining unit, Memphis Sand, almost completed sampling well in window (unconfined) region.



October 2002: Eager to sample, but way too much water!



November 2002: Oh-oh, still way too wet! A stout cable and big tractor to the rescue.



November 2002: A little sun and the right equipment lets us set-up at the window site.



Finally, serious sampling: Clockwise from upper left. Unloading at window well nest, slowly lowering pump and purging in preparation to collection, planning next step, sampling from one of three down-gradient confined locations.



Figure 8. Water Collection in Northeastern France

Sampling water seeping from limestone walls at 280 m depth during excavation to 490 m at Nuclear Waste Repository laboratory. Clockwise, from upper left: The excavation site, winches, suiting up, explosion debris bucket used to lower supplies, going down, inserting sampler in 3 m boring in limestone wall, and collecting for Kr-81. Inset: Collecting from 660 m depth at one of three surrounding off-site monitoring wells.